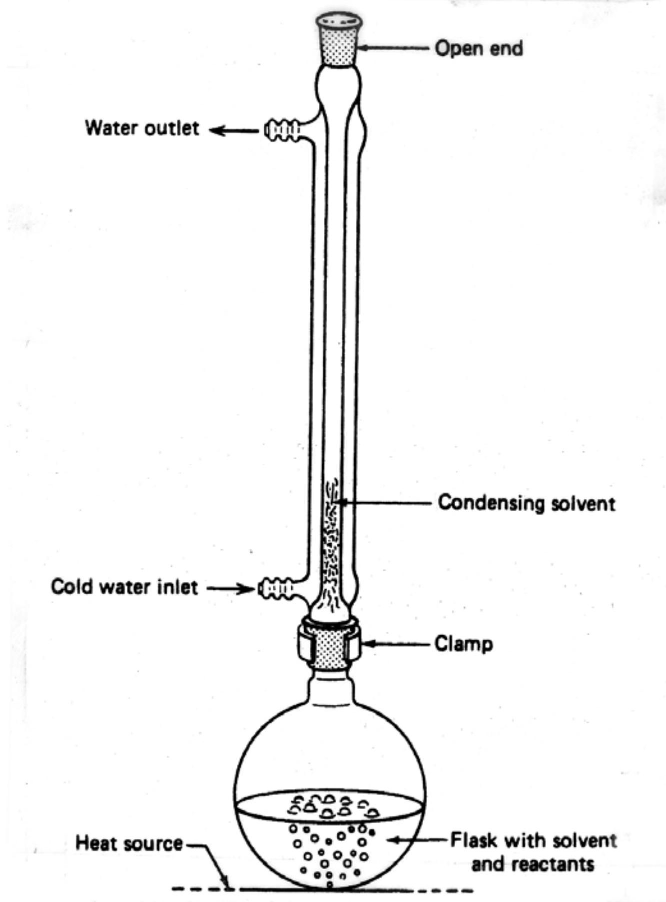
Otto Diels and his pupil Kurt Alder received the Nobel Prize in 1950 for their discovery and work on the reaction that bears their names. Its great usefulness lies in its high yield and high sterospecificity. The Diels-Alder reaction has been employed extensively in the synthesis of complex natural products because it is possible to exploit the formation of up to four asymmetric carbons in one reaction and at the same time it is also possible to control the regioselectivity of the reaction.

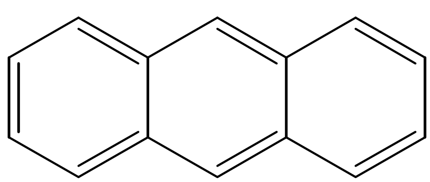
Many chemical reactions are done under reflux. By refluxing a reaction in a particular solvent, the reaction is kept at a constant temperature in a constant state of mixing. The boiling point of the solvent determines the reaction temperature. The solvent is boiled out of the reaction solution but quickly condenses and returns to the flask once the solvent vapors enter the reflux condenser. Chapter 22 of Zubrick addresses the topic of reflux.



A reflux setup.

Reference: "Experiments in Organic Chemistry" 2nd ed. (2000)
R.K. Hill & J. Barbaro,
Contemporary Publishing Company of Raleigh, Inc.

We will be performing the Diels Alder reaction with a very popular dieneophile – maleic anhydride. The diene we will be using is anthracene - a polycylic aromatic hydrocarbon (PAH) that can be found in coal, petroleum, and charcoal grilled hamburgers. The interesting aspect of anthracene is that it offers several different diene sites for the Diels Alder addition of maleic anhydride. Careful analysis of the product will allow us to determine the favored site of addition.



anthracene

## Procedure:

### A. Reaction and Isolation of Products

1. Add 2 g of anthracene to a 100 or 250mL round bottom flask.

2. Add 1 g of maleic anhydride to the round bottom. Despite its benign appearance, solid maleic anhydride is toxic and should not be handled with bare hands.

3. Add 25 mL of xylene (dimethyl benzene) to the round bottom. Do not remove the xylene bottle from the fume hood. Do this operation in the hood!

4. Add three boiling chips to the round bottom. Swirl the reactants to mix. The solids will not totally dissolve at this time.

5. Attach the round bottom to a reflux condenser mounted on a ring stand. Attach water hoses as shown in the preceding diagram

6. Use a thermwell mounted on an iron ring to heat the solution. Heat the mixture to boiling, and then adjust the heat input so that the boiling is maintained at a steady rate.
7. Reflux for 25 minutes. Note any changes in the reaction mixture. Complement your “hood mate” on how nice he/she looks today.

**8.** Turn off the heat source. Carefully transferring the hot contents to a 50 or 150 mL beaker at this time will make to easier to remove the crystals that form.

**9.** Chill in an ice bath.

**10.** Vacuum filter the solid (crude) product in a vacuum (Buchner) funnel. You may wash it with a small amount of ice-cold xylene.

**11.** Remove boiling chips with a tweezers.

**12.** Admire and the crude product.

### B. Recrystallization

1. Recrystallize your crude product with hexane.

2. Weigh and calculate % yield after it has had a chance to dry in your drawer.

3. Hand in a properly labeled sample of your product:

| |
|---|
| your name<br>date<br>lab title<br>product identity |

### C. Clean up.

1. Dispose of xylene filtrates in the proper container.

<u>Checklist for completing the "Prelab" section:</u>

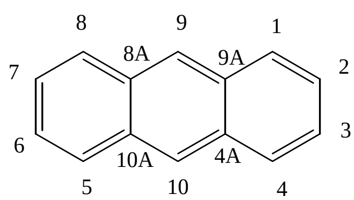
____ *Title*.

____ *Purpose*.

*Physical constants*. A table of physical constants and safety data for the chemical compounds referred to in the procedure is found on the CHEM254lab website: <http://domin.dom.edu/faculty/jbfriesen/chem254lab.htm>

____ *Structures and equations*.

1) There are 9 pairs of conjugated dienes in anthracene (for example [6,7,8,8A], [8,8A,9,9A], …). Which five have the required s-cis conformation?




numbering system for anthracene

2) Bearing in mind the pairs of conjugated dienes in question 1), what product is most likely to be formed? Draw the complete molecular structure please.
3) Reagent grade xylene is a mixture of 3 constitutional isomers. Draw the structures for these isomers.

___ *Flowchart.* Refer to "Procedure"

___ *Calculations.*

1) Calculate the number of moles in 2 grams of anthracene.
2) Calculate the number of moles in 1 gram maleic anhydride.
3) Calculate the theoretical yield of your predicted product.
4) Calculate the atom economy of the reaction. (Go to course webpage for summary of atom economy.)

____ *Safety Question*: You spill about 10 ml of xylene on the counter (outside of the hood!) when you are pouring it into your 50 mL graduated cylinder (step A.3). What two things should you do immediately?

**Experimental Observations and Data**:

Hand in a copy of your experimental observations and data before you leave lab.

*Experimental Observations*: Refer to Laboratory Syllabus for guidelines.

*Raw Data:* Refer to Laboratory Syllabus for guidelines.

**Lab Report Checklist**:

*Results*.

____ % yield of product → crude product mass x 100/theoretical yield. Show your calculations.

____ Interpret the IR spectrum, match the relevant functional groups on the molecule to the IR peaks.

____ What is the structure of your product? Use the $^{13}C$ and $^{1}H$ NMR data to confirm your proposal.

____ The $^{13}C$ NMR spectra is reported as follows: Interpret the $^{13}C$ NMR spectrum, match each carbon on the molecule to the appropriate $^{13}C$ NMR peak. Use the numbering scheme in Prelab question 1).

| Chemical shift (δ) in ppm | multiplicity |
|---|---|
| 48 | doublet |
| 56 | doublet |
| 125 | doublet |
| 126 | doublet |
| 143 | singlet |
| 215 | singlet |

____ Interpret the $^{1}H$ NMR spectrum for the product, give chemical shift, number of hydrogens, and multiplicity of each peak. Use the numbering scheme in Prelab question 1).

*Discussion and Conclusion*.

____ Is the product a chiral molecule? Why or why not?

____ What Diels Alder Reaction would you like to try (in the lab)? Write the complete structures in your equation.

____ What is one "Green Chemistry" advantage of this reaction?